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PTO 91-4925

Patent Application No. 6803739

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A PROCESS FOR THE PREPARATION OF MACROPOROUS POLYMERS
Czechoslovakian Academy of Sciences

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. OCTOBER 3, 1991

It is known that as a result of the copolymerization of styrene with divinylbenzene in the presence of liquids that dissolve the monomers, but not the copolymer, macroporous copolymers, (copolymers with visible porosity), are formed. Copolymerization of hydrophilic monomers, such as, for example, ethylene glycol monomethacrylate with ethylene glycol bismethacrylate [sic; bismethacrylate] in the presence of more water than the copolymer that is formed, more than can be absorbed by swelling, yields a sponge-like hydrogel with very fine capillary pores. The pores disappear forever after drying, and they cannot be recovered by allowing them to swell once again in water. The copolymer remains vitreous and transparent, without having visible porosity. This state of affairs renders the porous hydrophilic copolymers unusable for many purposes that require repeated sorption, such as, for chromatography, for filtering nonaqueous liquids, and others. The preparation of such sponge-like copolymers was described, for example, in the U.S. Patent Nos. 2,976,576 and 3,220,960.

The invention has as its goal the creation of hydrophilic copolymers of the aforementioned type that have a lasting macroporous (macroreticular) structure. In keeping with another embodiment of the invention, hydrophilic, macroporous copolymers on site in tubes or other containers are formed as a result of copolymerization, as a result of which nonleaking sorption columns and analogous facilities can be obtained.

Hydrophilic properties are favorable for certain goals, such as, for example, for the separation of polar and nonpolar compounds, for the preparation of detectors of polar compounds in gas analysis, and so forth.

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The process in keeping with the invention consists of the fact that bifunctional monomers that can be polymerized, such as, for example, ethylene glycol monomethacrylate or -acrylate, together with a crosslinking agent that is soluble in the monomer mixture, such as, for example, ethylene glycol bismethacrylate or N,N'-methylene bismethacrylamide, without significant quantities of water or another strongly polar substance, and in the presence of a liquid that dissolves the monomers to a homogeneous phase, without, however, dissolving the copolymer that is formed, or allowing it to swell, are polymerized, or copolymerized, respectively. -

Typical examples of liquids that do, indeed, dissolve monomers but not the copolymer, are aromatic hydrocarbons, such as benzene, toluene, xylene, and so forth. It is possible however, to use many esters, chlorinated hydrocarbons, ethers, ketones, high-molecular weight aliphatic alcohols, cycloaliphatic alcohols, and other substances with analogous results. In addition, many macromolecular substances, such as polyvinyl alcohol, for example, silicone oils, polyesters, polyethylene glycols, and others, may be used for this purpose.

Macroporous, hydrophilic polymers, or copolymers, respectively, which are prepared in a manner as described above, differ considerably from the spongy hydrogels that have been known thus far. Their pores are larger, and they do not disappear in the drying process. The material does not lose its sorption properties as a result of this, not even if it is allowed to swell and dry repeatedly. The new macroporous,

hydrophilic copolymers can thus, for example, serve as substrates for the anchored phase in the gas-liquid chromatography, or as inert substrates for various catalysts, as sorption and filtration materials, primarily in nonaqueous environments.

If the copolymerization in the aforementioned manner, is conducted in a suitable mold, such as a tube, or some other structural vehicle, the result is various ready-to-use sorption systems that have an arbitrary selection of shapes and sizes, and fill the entire cross section of the sorption device. A sorption column prepared in this way has no dead space and is very effective. No wear occurs, not even after long-term operation, which is quite the opposite of the usual granular fillers..

By the addition of liquids that can permit the hydrophilic copolymer to swell, the size of the pores, or the structure of the pores, respectively, are controlled, and thus adjusted to each desired special application. Swelling agents of this type include, for example, low molecular weight aliphatic alcohols, such as methanol, ethanol, or propanol, also allyl alcohol, tetrahydrofurfuryl alcohol, ethylene glycol, polyethylene glycol, homologous glycols, glycol ethers, tetrahydrofuran, formamide, dimethylformamide, pyridine, dimethyl sulfoxide, and others.

The monomers that may be used in accordance with the process in keeping with the invention, may also contain ionogenic groups, or groups of that kind can be added to the polymer later. It is therefore possible, for example, to add a certain quantity of methacrylic or acrylic acid, maleic anhydride, itaconic acid, an ester or a salt of ethenesulfonic acid, etc., to the monomer mixture that in the main consists of ethylene glycol monomethacrylate, or the like.

In addition to glycol acrylates and glycol methacrylates, it is also possible to use other hydrophilic monomers, such as, for example, acrylamide, methacrylamide, monoacrylates of polyvalent alcohols, such as glycerol, pentaerythritol, mannitol, and other sugars. Dimethyl acrylates, and acrylates, respectively, of the polyvalent alcohols, can be used as crosslinking agents.

The quantity of crosslinking agents can vary within broad limits, depending upon the property of the product that is desired, and the application for which it is intended. In small quantities of the crosslinking agent, such as, for example, below 2 wt%, copolymers are obtained that swell to a pronounced degree in water and polar solvents. In the case of an elevated quantity of crosslinking agent, the capacity to swell decreases, and strength and toughness in the swollen state increase. For special purposes, it is also possible to use crosslinking agents with long chains, such as, for example, dimethyl acrylates, and polyethylene glycols having an average molecular weight of 1500-3000. By skillful combinations of the length of the chain with the crosslinking agent, the quantity thereof (the molar fraction with respect to the basic monomer), and the quantity of inert liquid that causes the microporosity, it is possible to prepare a whole series of materials having various properties for chromatography, filtration, sorption, or other purposes.

The smallest quantity of the liquid that causes the porosity depends upon the properties of the liquid itself, and also upon the nature of the monomer that is used, and upon the quantity of crosslinking agent. If aromatic hydrocarbons are used, the

smallest effective quantity is approximately 20 wt%. The upper limit is determined by the degree of strength that is desired, which strength diminishes as the quantity of inert liquid increases.

If less than the minimum effective quantity of inert liquid is added, what is obtained after drying is just the usual vitreous, nonporous structure.

If, instead of taking place directly in a tube or similar "in situ" filling, polymerization occurs in a mold or in a vat, a block is obtained that is used in that state, or subsequent to breaking and sorting. It is also possible to undertake polymerization in the form of the usual suspension polymerization by means of a suspension environment, using, for example a saturated, aqueous sodium chloride solution that has 0.5-3 wt% magnesium hydroxide added as a stabilizing medium, as a suspension.

To prepare a column with a solid filling of a hydrophilic macroporous polymer, it is possible to proceed in the manner outlined below.

To a tube of suitable size that is made of metal or glass, a homogeneous solution of a hydrophilic monomer, such as, for example, ethylene glycol monomethacrylate is added, as well as a suitable quantity of a crosslinking agent, such as, for example ethylene glycol bismethacrylate, in a solvent, such as toluene, in which the polymer that is formed neither swells nor dissolves. To the solution, an polymerization initiator is added, such as, for example, 0.3 wt% diisopropyl percarbonate, and it is poured into the aforementioned tube, which is closed at the bottom. The polymerization is then performed at a suitable temperature. In

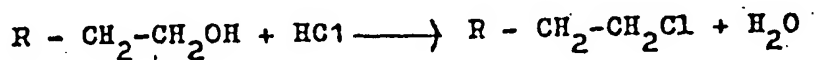
the case of bisdiisopropyl percarbonate, 1 hour of heating to 60°C is sufficient; with some redox initiators (such as cumene hydroperoxide p-toluenesulfinic acid, perhaps in the presence of a small quantity of complex copper salts), polymerization will occur without any heating.

Toluene or another solvent for the monomer is then rinsed with anhydrous ethanol, which is finally replaced by a liquid that is used as the stationary phase in the gas-liquid chromatography, for example, by ethylene glycol monomethyl ether.

If the quantity of solvent is quite small (for example 30-60 wt%), the filling is self-supporting, and it is not necessary to use a bottom made of sintered glass or another porous material.

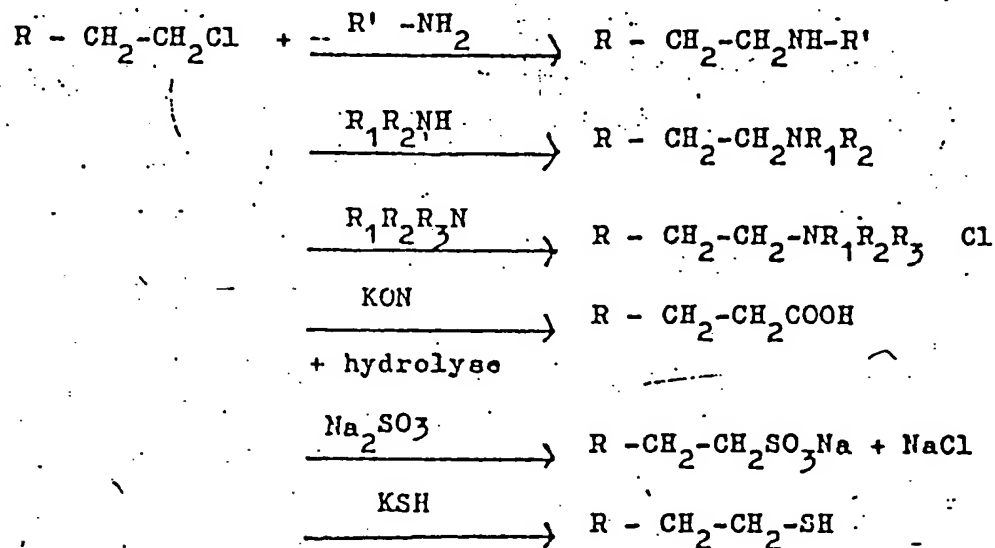
Columns made of macroporous hydrophilic material can also be prepared in such a way that a mixture having quite a small quantity of solvent is polymerized in a mold into a column or staff, and then it is supplied with a mantle made of a plastic or metallic plate.

Prepared macroporous hydrogels in keeping with the invention can also be modified later by suitable chemical reactions. It is thus possible, for example, to cause macroporous hydrogels made of ethylene glycol monomethacrylate to react with thionyl chloride or hydrochloric acid, as a result of which, a polymer chlorohydrin ester in keeping with the reaction scheme outlined below is obtained:



in which R represents a methacrylic acid residue.

The polymeric chlorohydrin can, for example, serve as a carrier for chromatography in a water-free environment, or as an intermediate product for additional reactions, such as those in keeping with the reaction scheme below:



In an analogous way, it is possible to obtain other derivatives of the polymer by the direct effects of the reagents on the macroporous polymer, such as, for example, thiocyanates, thiuronium salts, sorbents for humic acids, etc.

Macroporous polymers or copolymers in keeping with the invention, can thus be applied in a variety of ways, for example, as chromatographic sorbents, skeletons for ionic exchangers, sorbents for various organic substances (such as, for example, for the isolation and removal of antibiotics), catalytic carriers, materials for the filtration of gels, etc. In comparison with the known materials, such as, for example, dextran derivatives, these substances have the advantage that

they are resistant in acidic, as well as in basic environments. Thus, for example, macroporous ethylene glycol monomethacrylate, which is crosslinked with ethylene glycol bismethacrylate at 20°C, is not affected by hydrochloric acid or sodium hydroxide, up to a concentration of 20 wt%.

Example I

150 ml of toluene, 17.4 ml of ethylene glycol bismethacrylate, 332 ml of ethylene glycol monomethacrylate, and 0.05 g of dibenzoyl peroxide are mixed to a homogeneous solution, and pure nitrogen is allowed to bubble through this mixture. The polymerization is accomplished by heating to 50°C for a period of 6 hours under an atmosphere of nitrogen. The macroporous material that is obtained in this way is then broken up into granules, and the toluene is distilled off. The distillation may occur under reduced pressure, or, it may be accomplished using steam. The product can be separated with the help of sieves, and be used as a filling for sorption columns.

In an analogous way, analogous copolymers of diethylene glycol or triethylene glycol monomethacrylate using various crosslinking agents, such as, for example, glycerol trimethacrylate, or N,N-methylenebismethacrylamide, are prepared. The quantity of crosslinking agents can vary within wide limits. The porosity is dependent upon the quantity of toluene or the like that is used.

Example II

150 ml of benzene, 20 ml of ethylene glycol bismethacrylate, 350 ml of ethylene glycol monomethacrylate, and 0.08 g of diisopropyl percarbonate are mixed to a homogeneous solution. The solution is then poured into a polytetrafluorethene tube, and heated from the outside to 60°C. When the copolymerization has run to completion, the benzene is removed by anhydrous ethanol, which is then replaced by ethylene glycol monomethyl ether. The filled column that is obtained in this way is used for gas-liquid chromatography.

Example III

Into a cylindrical reactor that is equipped with a mixer, 41.1 g of magnesium sulfate heptahydrate are dissolved in 110 g of water. Then a solution of 11.31 g of sodium hydroxide in 31.25 g of water is added, stirring all the while. In this way, a suspension of 1.5 wt% magnesium hydroxide is obtained in the salt solution, in which a monomer solution of 48.42 ml of ethylene glycol monomethacrylate and 4.98 ml of ethylene glycol bismethacrylate is suspended in 25 ml of toluene, mixing all the while. After 10 minutes of mixing at 25°C, the temperature is increased to 60°C. In the course of two hours, solid granules of macroporous copolymer are formed. The copolymerization is allowed to run its full course by three hours of mixing at the same temperature. Then the magnesium hydroxide is dissolved by the addition of a nearly equivalent quantity of hydrochloric acid; the suspended polymer is filtered off, washed with water,

and dried. The size of the granules can be easily adjusted by changing the number of revolutions, and by the quantity of magnesium hydroxide. Smaller granules can be obtained at higher numbers of revolutions, and with a greater quantity of magnesium hydroxide.

Example IV

A homogeneous mixture of 7.5 ml of toluene, 6.005 ml of ethylene glycol monomethacrylate, 1.495 ml of ethylene glycol bismethacrylate, and 0.1 g of dibenzoyl peroxide is poured into a tube with a melted glass bottom that measures 5.3 mm in diameter. The polymerization process takes 3 days at 28°C. The melted bottom is then cut off and the polymer column is washed, first with methanol, then with water. The column may be used as a sorbent for analytical purposes.

Example V

By pouring a solution of 4.78 ml of ethylene glycol bismethacrylate, 19.72 ml of ethylene glycol monomethacrylate, and 0.35 g of dibenzoyl peroxide in 10.5 ml of toluene into a cylindrical mold, a microporous polymer in the form of a staff is prepared. The mold is made out of Woods metal, such that a reaction tube is used as a porthole. The solution is first bubbled with pure nitrogen, then heated to 50°C for 5 hours.

The metal is then melted away, and any residues of it are removed using toluene at 100°C. The staff of microporous polymer that is obtained in this way is then worked mechanically to the desired shape, the toluene is then washed out with methanol and the methanol is then removed, as a result of evaporation in a warm current of nitrogen that is drawn through the polymer.

Example VI

The preparation of polymers, macroporous chlorohydrin ether.

78 g of macroporous copolymer in granular form measuring 0.2-0.5 mm are suspended in 250 ml of thionyl chloride and the suspension is boiled for four hours under reflux cooling. Then 1 ml of anhydrous pyridine is added and the suspension is boiled for an additional 2 hours. Then, the excess thionyl chloride is distilled off, the copolymer is washed with benzene, and the latter is removed in boiling water. The yield amounts to 80 g of chlorinated copolymer having a content of 21.5 wt% chlorine. The chlorohydrin polymer can be used as a sorbent in nonaqueous liquids.

The chlorine content of the product depends upon the degree of crosslinking. In an analogous example with only 2 wt% ethylene glycol bismethacrylate, the chlorine content increases to 23 wt%; with 20 wt% of the same crosslinking agent, however, the chlorine content declines to 18.5 wt%.

Example VII

80 grams of the polymeric, macroporous chlorohydrin ether, in the form of granules measuring 0.2-0.5 mm are immersed in 500 ml of ethanol, and brought to a boil, stirring all the while. Then 494 grams of m-phenylenediamine are added and the suspension is boiled for 35 hours under reflux cooling. By drawing off, then washing with methanol, followed by a 1% solution of hydrochloric acid, then with a 1% solution of sodium hydroxide, and finally with water, an aminized copolymer with a nitrogen content of 9.92 wt% is obtained. Analogous results are obtained using m-toluenediamine.

Example VIII

100 grams of polymeric, macroporous chlorohydrin ether that is prepared in accordance with Example VI with 20 wt% of a crosslinking agent, and which contain 18.2 wt% chlorine, are heated with 1000 ml of a 30-solution [sic] of trimethylamine in water for a period of 8 hours to 60°C. The aminized copolymer is then washed with a 5% solution of hydrochloric acid and dried at 20°C. The nitrogen content amounts to 3.94 wt%. The aminization can be rendered easier by the addition of aromatic hydrocarbons to the aqueous amino solution. If, for example, the aminization of a macroporous polymeric chlorohydrin ether that is prepared with 20 wt% crosslinking agent, an ether containing 15.5 wt% chlorine, is carried out over a period of 8 hours at 60°C, a

polymer with only 1.82 wt% nitrogen is obtained. In an analogous test under the same circumstances, but without the addition of toluene, the nitrogen content in the product increases to 3.5 wt%.

Claims

1. A process for preparing macroporous polymers and copolymers by polymerization in the presence of a liquid, in which the monomer, or monomers, respectively, is/are soluble, but in which the polymer or copolymers that is/are formed, respectively, is/are not soluble, characterized by the fact that a hydrophilic monomer with a double bond that is capable of polymerization, such as, for example, ethylene glycol monomethacrylate, is polymerized or copolymerized with a crosslinking agent, such as, for example, ethylene glycol bismethacrylate, in an anhydrous state, and in the presence of an inert liquid that readily dissolves the monomeric material, in which the polymer or copolymer that is formed is insoluble, and, by its nature, incapable of swelling.

2. A process in keeping with Claim 1, characterized by the fact that the polymerization or copolymerization is conducted in a tube, and the column formed in this way is liberated of the inert liquid by its evaporation or extraction.

3. A process in keeping with Claim 1 or 2, characterized by the fact that for the purposes of polymerization, a small quantity of liquid is added in which the polymer or copolymer that is formed is capable of swelling.

4. A process in keeping with Claims 1-3, characterized by the fact that an aromatic hydrocarbon is used as an inert liquid.

5. A process in keeping with Claims 1-4, characterized by the fact that one or more reagents is allowed to work on a polymer or copolymer prepared in keeping with Claims 1-4.

6. A process in keeping with Claim 5, characterized by the fact that thionyl chloride is allowed to work on a polymer or copolymer prepared in keeping with Claims 1-4.

7. A process in keeping with Claim 5 and 6, characterized by the fact that first thionyl chloride, and then an amine is allowed to work on a polymer or copolymer prepared in accordance with Claims 1-4.

8. Objects obtained as a result of applying the processes in keeping with Claims 1-7.

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